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OSCILLATOR STRENGTH OF THE CN VIOLET SYSTEM

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ABSTRACT

The electronic oscillator strength, f , for the CN violet system was determined by measuring the radiation from the shock layer about a hypervelocity projectile with a time-of-flight scanning spectrometer. The measured values at the $\Delta v = +1$ and $\Delta v = -1$ band sequences were $f = 0.019 \pm 0.004$ and $f = 0.020 \pm 0.004$, respectively, assuming a heat of dissociation ΔH_0° for CN of 8.2 ev. A parametric analysis of the radiation observed as a function of projectile velocity indicated that a ΔH_0° for CN of between 8.1 and 8.4 ev gave the best representation of the data.

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NOMENCLATURE

a_0	radius of Bohr orbit (cm)
c	velocity of light (cm sec ⁻¹)
d	degeneracy of electronic state, dimensionless
e	charge of electron (esu)
f	electronic oscillator strength, dimensionless
$f_{v',v''}$	band oscillator strength, dimensionless
ΔH_0^0	heat of dissociation (ev)
h	Planck's constant (erg-sec)
I	calculated radiant power from a band (watts-cm ⁻³)
J	calculated radiant power from a band sequence as seen by spectrometer (watts)
m	mass of electron (g)
N	particle density (cm ⁻³)
P_∞	free-stream pressure (mm Hg)
$q_{v',v''}$	Franck-Condon factor, dimensionless
R_∞	Rydberg constant (cm ⁻¹)
R_e	electronic transition moment (cm ² esu ²)
v	vibrational quantum number, dimensionless
W	measured radiant power from a band sequence as seen by spectrometer (watts)

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λ	wavelength (cm)
ν	wave number (cm^{-1})
ρ	density (g-cm^{-3})
τ	volume (cm^3)

I. INTRODUCTION

It was shown in a previous paper⁽¹⁾ that reliable values of oscillator strengths (f-numbers) may be obtained by measuring the radiation from the shock layer about a hypervelocity projectile with a time-of-flight scanning spectrometer. The current work is an application of this technique to the CN violet $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ system. Recent interest in radiation from CN stems from the possibility that the atmospheres of Mars and Venus contain CO_2 and N_2 .⁽²⁾ If this is correct, the CN radical will be formed in sufficient quantity in the shock layer of vehicles entering these atmospheres at high speeds so as to be a major source of radiative heating. Thus, if reasonable radiative heating predictions are to be made for such entry vehicles, both the number of CN radicals formed in the shock layer and accurate f-numbers are required.

II. EXPERIMENTS

The experimental setup was identical to that described in reference 1. Polyformaldehyde models were launched from the two-stage, shock-heated, 0.28-caliber-light-gas gun of the pilot

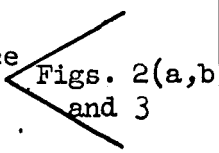
hypervelocity free-flight facility at the NASA Ames Research Center. Model velocity and attitude were measured by means of shadowgraphs and electronic counters. Continuously recorded photoelectric spectra were obtained with a time-of-flight scanning spectrometer (Fig. 1). The spectrometer works on the principle that as the model flies by in the focal plane of the collecting mirror, the luminous gas cap acts as a moving entrance slit, sweeping out the spectrum of the shock-heated gas on the exit slit. The energy passing through the exit slit falls on the cathode of an RCA 1P28 multiplier phototube, the output of which is recorded on an oscilloscope.

Fig. 1

The test gases were mixtures of CO_2 and N_2 : 4 per cent, 9 per cent, and 25 per cent CO_2 ; remainder N_2 . Samples of the gas were taken immediately prior to shooting and analyzed with a CEC 21620 mass spectrometer. All contaminants (O_2 , A, water vapor) were held to below 0.3 per cent, and no noticeable effect was observed with this degree of contamination.

Spectrometer oscillograms were obtained for a range of model velocities of from 3.7 to 4.9 km/sec and ambient pressures of 60 and 90 mm Hg for the various mixtures. Figure 2(a) shows a typical oscillogram and Fig. 2(b) is this oscillogram reduced to absolute levels. Calibration and experimental data reduction procedures are discussed in reference 1.

In addition to the spectrometer measurements, several photographic spectra of the luminous gas cap, as observed perpendicular to the flight path, were taken by Mr. Ellis E. Whiting of Ames Research Center.

One of these is reproduced as Fig. 3. Note the complete predominance of the CN violet system, in agreement with the spectrometer result. 

The spectrograph was a Huet UV 24, which is a dual prism F/3.5 instrument.

III. CALCULATIONS

The electronic oscillator strength was determined by fitting the measured power radiated from each band sequence to a synthetic spectrum. The synthetic spectra were calculated using the methods described in reference 1, with the appropriate constants for the CN violet system. Thermodynamic properties and specie concentrations were calculated using the program developed by BAILEY,⁽³⁾ spectroscopic constants were from HERZBERG,⁽⁴⁾ the Franck-Condon factors were taken from NICHOLLS,⁽⁵⁾ and the spectral distribution was obtained by the method of WILLIAMS and TREANOR.⁽⁶⁾ The main assumptions are that the gas in the shock layer is inviscid, in thermodynamic equilibrium, can be considered optically thin and that the shape of the bands can be adequately represented by an averaged Q branch.

It has been observed in several places^(7,8) that the use of "electronic f-numbers" has been the cause of some confusion. In view of this, it is worthwhile to write out explicitly what is meant here (at least) by the electronic f-number in terms of what was measured. The radiation per unit volume from a given electronic-vibrational band may be written*

*For simplicity the effect of induced absorption is neglected in this discussion, but was included in the calculation.

$$I = \frac{8\pi^2 h e^2}{m c^3} N_{v'} \nu^3 f_{v', v''} \quad (1)$$

where $N_{v'}$ is the number density of the radiating molecules in the upper v' state, ν is a mean wave number for the $v' - v''$ transition, and $f_{v', v''}$ is the band oscillator strength. Thus, for any band sequence, i.e., those bands whose vibrational quantum number difference $v' - v''$ is a constant

$$\sum_{\Delta v = \text{const}} I = \frac{8\pi^2 h e^2}{m c^3} \sum_{\substack{v' \\ \Delta v = \text{const}}} N_{v'} \nu^3 f_{v', v''} \quad (2)$$

If W is the energy radiated per second from a band sequence as measured in the current experiments, then

$$W = \frac{8\pi^2 h e^2}{m c^3} \int_{\text{vol}} \left[\sum_{\substack{v' \\ \Delta v = \text{const}}} N_{v'}(\rho, T) \nu^3 f_{v', v''} \right] d\tau \quad (3)$$

where the integration is taken over the volume of the shock layer seen by the spectrometer. At this point one can write $f_{v', v''}$ in terms of the band strength $R_e^2 q_{v', v''}$

$$f_{v', v''} = \frac{\nu}{3R_\infty d'} \left(\frac{R_e}{e a_0} \right)^2 q_{v', v''} \quad (4a)$$

where R_e is the electronic transition moment, $q_{v', v''}$ is the Franck-Condon factor, and d' is the degeneracy of the upper state. The band oscillator strength is also written in terms of the electronic f-number⁽⁹⁾

$$f_{v', v''} = f q_{v', v''} \quad (4b)$$

Substituting equation (4a) or (4b) into equation (3) and further assuming that f or R_e^2 does not vary appreciably over a band sequence yields

$$\left(\frac{R_e}{ea_0}\right)^2 = W \frac{8\pi^2 d' h e^2}{3R_\infty m c^3} \int_{vol} \left[\sum_{\substack{v' \\ \Delta v = \text{const}}} N_{v'}(\rho, T) \nu^4 q_{v', v''} \right] d\tau \quad (5a)$$

and

$$f = W \frac{8\pi^2 h e^2}{m c^3} \int_{vol} \left[\sum_{\substack{v' \\ \Delta v = \text{const}}} N_{v'}(\rho, T) \nu^3 q_{v', v''} \right] d\tau \quad (5b)$$

The assumption of constant f or R_e^2 over a band sequence should be particularly good for the CN violet system since the wavelength extent of the band sequences is small.

The only virtue for using the f -number rather than the electronic transition moment is that the f -number is in general use and therefore allows a more direct comparison between different experiments. On the other hand, there are conceptual difficulties when defining an electronic f -number for a complete band system. In particular the relationship between the electronic f -number and the classical definition of the f -number (i.e., the fraction of the optical electron associated with the transition) has little significance. In this context the f -number should perhaps be thought of as simply the ratio of the band oscillator strength $f_{v', v''}$ to the Franck-Condon factor $q_{v', v''}$. A useful critical review of the subject is given by NICHOLLS and STEWART.⁽⁷⁾

IV. RESULTS AND DISCUSSION

The oscillator strength cannot be determined from any one of the present experiments unless the number density of CN radicals is known (cf. eq. (5)). Unfortunately, at present there exists in the literature a wide range of heats of dissociation, ΔH_O^0 , for CN, none of which is clearly better than any other. Thus, there remains considerable uncertainty as to the correct CN number densities. It is possible, however, to determine a fairly precise oscillator strength for any one ΔH_O^0 , and then consider what values of ΔH_O^0 fit the data best over the complete range of experiments. This is the attack chosen for the present work.

The f-numbers for the $\Delta v = +1$ ($\lambda \sim 3560 \text{ \AA}$) and $\Delta v = -1$ ($\lambda \sim 4170 \text{ \AA}$) sequences were found to be $f = 0.019 \pm 0.004$ ($(R_e/ea_O)^2 = 0.45$) and $f = 0.020 \pm 0.004$ ($(R_e/ea_O)^2 = 0.56$), respectively, assuming a heat of dissociation for CN of 8.2 ev. The uncertainty here is deduced from data scatter plus estimates of possible systematic errors. The integrated radiant output of the two band sequences is shown in Figs. 4(a,b,c,d) as a function of projectile velocity for 9 per cent CO₂, 91 per cent N₂, and 4 per cent CO₂, 96 per cent N₂ at various ambient pressures. The curves represent integrated radiant output from the synthetic spectra with f-numbers calculated by applying the method of least squares to the data. The results include the subtraction of a generally small (less than 15 per cent) contribution due to the N₂(2+) and N₂⁺(1-) systems. The value of this

Figs. 4
(a,b,c,d)

contribution was estimated from shots in pure N_2 and the magnitude of the $\Delta v = +1$ and $\Delta v = +2N_2(2+)$ band sequences observable on the CN oscillograms.

In addition to the above, several shots into a mixture of 25 per cent CO_2 , 75 per cent N_2 gave essentially identical f-numbers.

It is worth noting that no measurable nonequilibrium contribution to the radiation from CN violet was observed. This can be inferred from the independence of the deduced f-number from the calculated, equilibrium shock-layer density. This is somewhat different from the case for the N_2 systems reported previously, where appreciable non-equilibrium radiation was observed at the lower shock-layer densities.

No f-number was determined for the $\Delta v = 0$ band sequence ($\lambda \sim 3860 \text{ \AA}$) as the assumption of optical thinness was clearly untenable for this sequence. This is shown in Fig. 5, which is a comparison of the reduced experimental spectrum of Fig. 2 with the synthetic spectrum calculated at the appropriate conditions. The black-body curve shown was calculated for a mean-shock-layer temperature and the f-number was taken as 0.02. Such self-absorption effects for the $\Delta v = 0$ sequence are also evident in Fig. 6, which compares the data, the calculated radiant output using $f = 0.02$, and the black-body curve as functions of velocity for one series of experiments.

The variation of the electronic transition moment from the $\Delta v = +1$ ($\lambda \sim 3560 \text{ \AA}$) to the $\Delta v = -1$ ($\lambda \sim 4170 \text{ \AA}$) band sequences was found to be $R_e(\Delta v = +1)/R_e(\Delta v = -1) = 0.90$. This differs from that reported by NICHOLLS,⁽¹⁰⁾ who obtained a relative variation in R_e

Fig. 5

Fig. 6

with r-centroid so that $R_e(\Delta v = +1)/R_e(\Delta v = -1) = 1.38$. Nicholls deduced this value from the band-head intensity measurements of ORNSTEIN and BRINKMAN.⁽¹¹⁾ If, on the other hand, Nicholls' method is applied to the measurements of TAWDE,⁽¹²⁾ as reported by FEAST,⁽¹³⁾ $R_e(\Delta v = +1)/R_e(\Delta v = -1)$ is about 0.80. The eye estimates of band-head intensity of PEARSE and GAYDON⁽¹⁴⁾ also support a lower value. While there always exists the possibility that the $\Delta v = -1$ band sequence measured here may be partially self-absorbed, this would seem unlikely, considering how the data for this sequence agree with the "optically thin" approximation over the range of experimental velocities (Figs. 4(a,c)). It would appear, then, that the bulk of the evidence points to a different variation of R_e with r-centroid than originally reported.

The results given here compare favorably with that of BENNETT and DALBY,⁽¹⁵⁾ who give $f = 0.027 \pm 0.003$ for the $\Delta v = 0$ sequence using an electron beam delayed coincidence method. The Bennett and Dalby result does not depend upon the choice of a ΔH_0^0 for CN. FAIRBAIRN,⁽¹⁶⁾ using a shock tube, obtained $f = 0.016 \pm 0.008$ for $\Delta v = -1$ assuming a heat of dissociation for CN of 8.35 ev. However, as Fairbairn points out, the number density of CN radicals and hence the f-number deduced from absolute emissive power measurements is quite sensitive to the heat of dissociation of CN for any experiment which relies upon thermal excitation to supply the CN. This is shown explicitly in Fig. 7 where the f-number determined by the present method is given as a function of the assumed ΔH_0^0 of CN. Figure 7

also includes some of the values for the ΔH_0^0 and f of CN currently reported in the literature. While any one measurement cannot determine both the ΔH_0^0 and f , some idea of the correct heat of dissociation can be obtained by observing the behavior of the present data as a function of model velocity, since the shape of this curve is dependent upon ΔH_0^0 . As an example of this, Fig. 8 shows the calculated value of $\int_{\Delta v=1}^{\infty} I \, dv = J$ as a function of projectile velocity for two different heats of dissociation. The best ΔH_0^0 will be that which fits the data closest over the complete range of the experiments. A measure of the quality of the fit is given by the sum of the square of the fractional residuals

$$\sigma = \sum_n \left(\frac{J - W}{W} \right)^2$$

where n is the number of data points. Figure 9 shows σ normalized to σ at $\Delta H_0^0 = 8.2$ ev as a function of ΔH_0^0 . While it is obviously impossible to pick one best ΔH_0^0 , the values of ΔH_0^0 between 8.1 and 8.4 ev would appear to give the most reasonable representation of the data. This would correspond to an f -number range of $f = 0.014$ to $f = 0.028$ (cf. Fig. 7). In view of these results, plus that of Bennett and Dalby, it would seem that a higher value of ΔH_0^0 is to be preferred.

Fig. 8

Fig. 9

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FIGURE CAPTIONS

Fig. 1.- Time-of-flight scanning spectrometer.

Fig. 2.- Experimental spectra. (a) Typical oscillogram from time-of-flight scanning spectrometer. (b) Reduced experimental spectrum.

Fig. 3.- Photographic spectrum of shock layer.

Fig. 4.- Variation of integrated shock-layer radiation from band sequences as a function of projectile velocity.

Fig. 5.- Comparison of experimental and synthetic spectra.

Fig. 6.- Effect of self-absorption on radiation observed by spectrometer for the $\Delta v = 0$ sequence.

Fig. 7.- Variation of measured f-number as a function of assumed heat of dissociation of CN for the $\Delta v = -1$ ($\lambda \sim 4170 \text{ \AA}$) band sequence.

Fig. 8.- Effect of assumed ΔH_O^0 on the shape of the J versus V curve.

Fig. 9.- Relative quality of the fit of J versus V to the data as a function of assumed ΔH_O^0 .

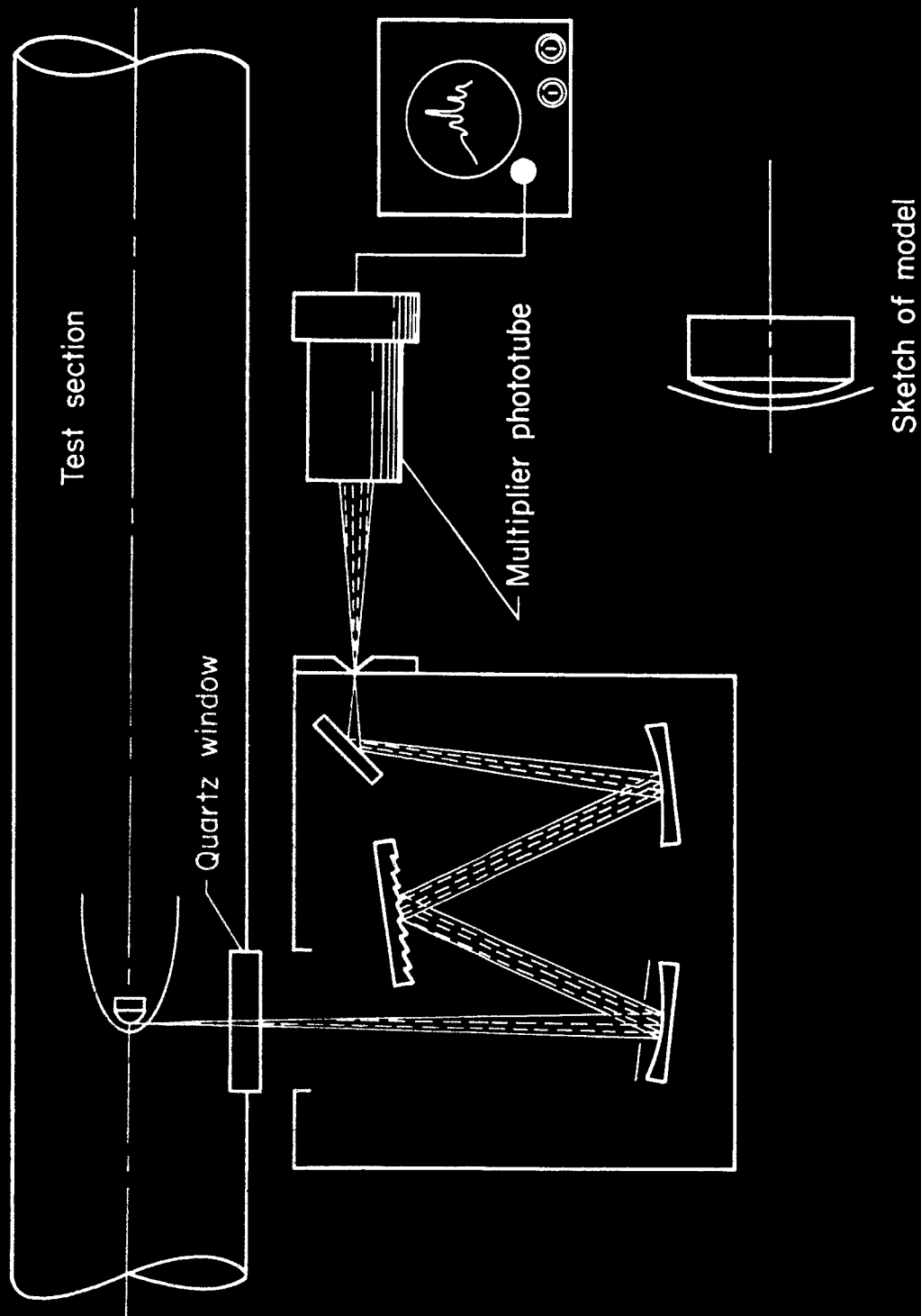
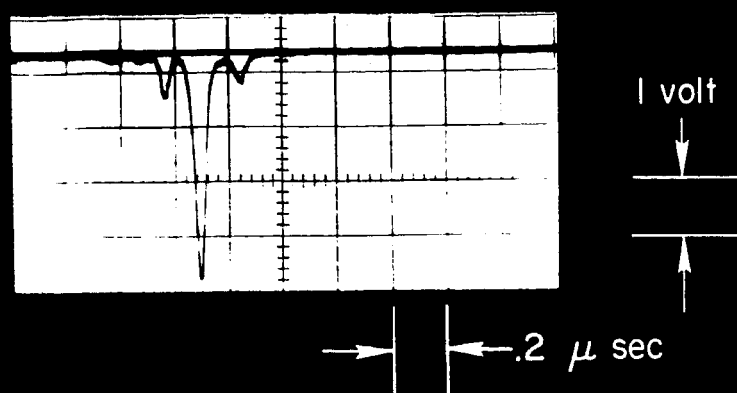
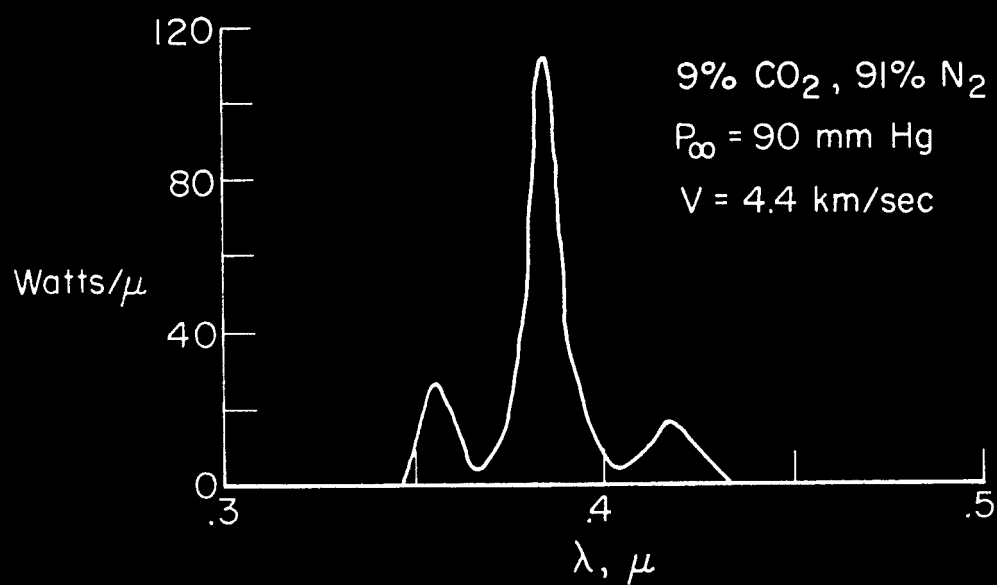


Fig. 1.- Time-of-flight scanning spectrometer.



(a) Typical oscillogram from time-of-flight scanning spectrometer.



(b) Reduced experimental spectrum.

Fig. 2.- Experimental spectra.

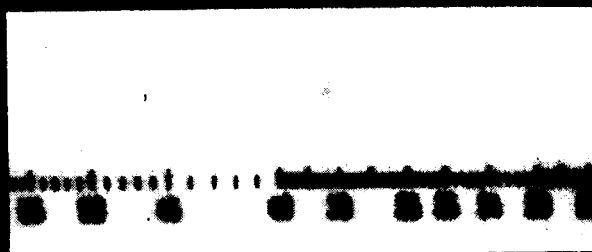


Fig. 3.- Photographic spectrum of shock layer.

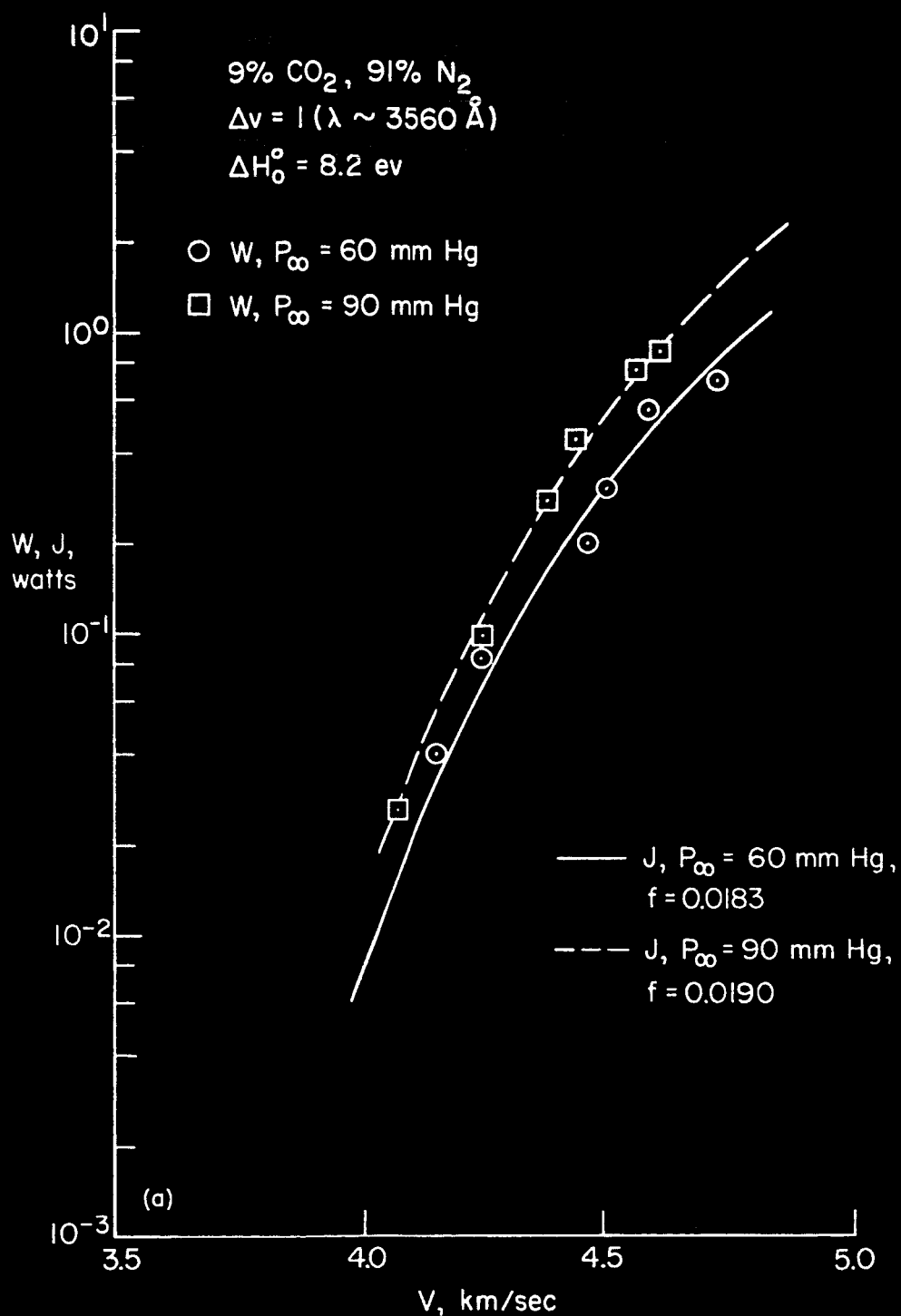


Fig. 4.- Variation of integrated shock-layer radiation from band sequences as a function of projectile velocity.

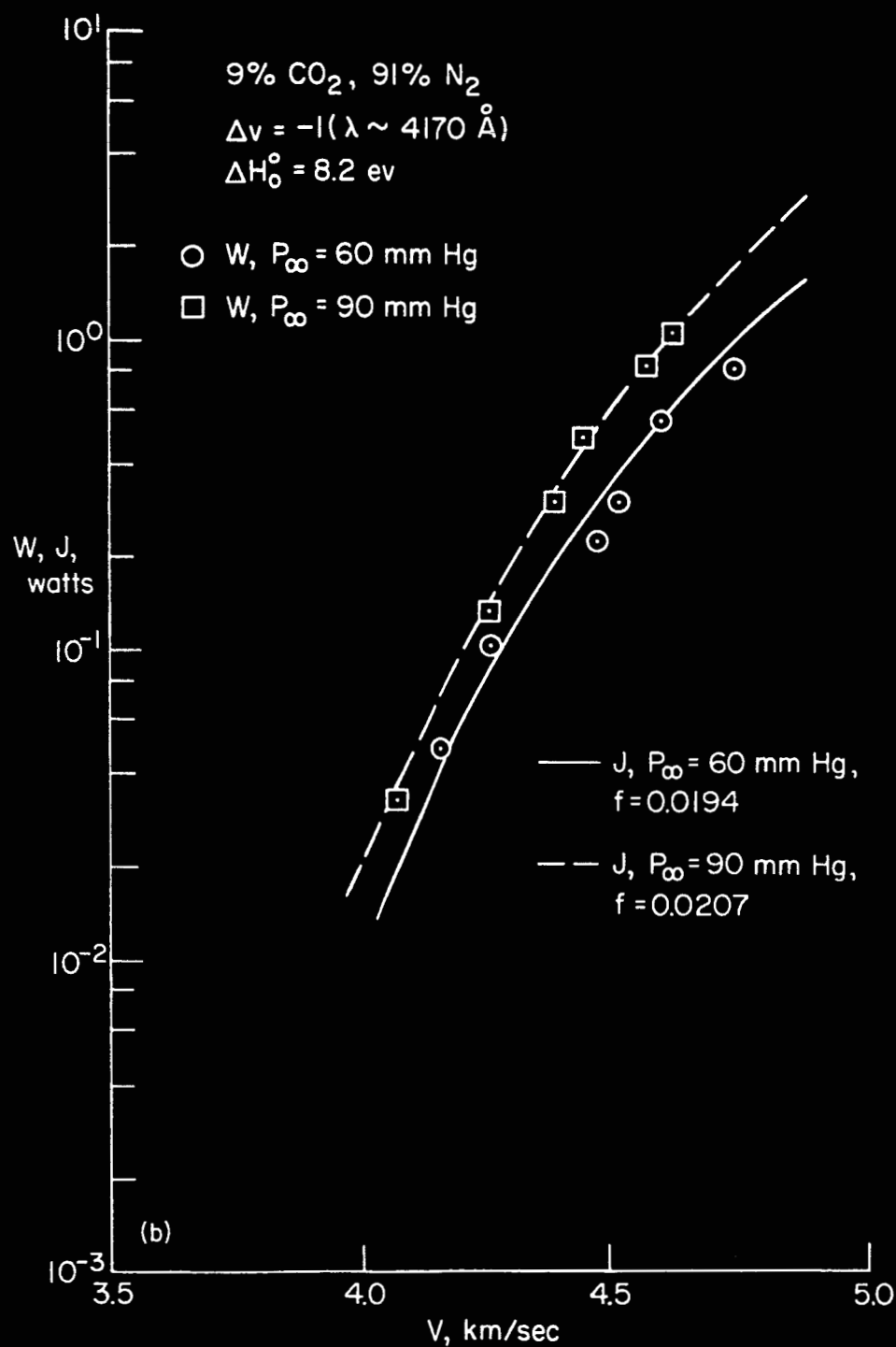


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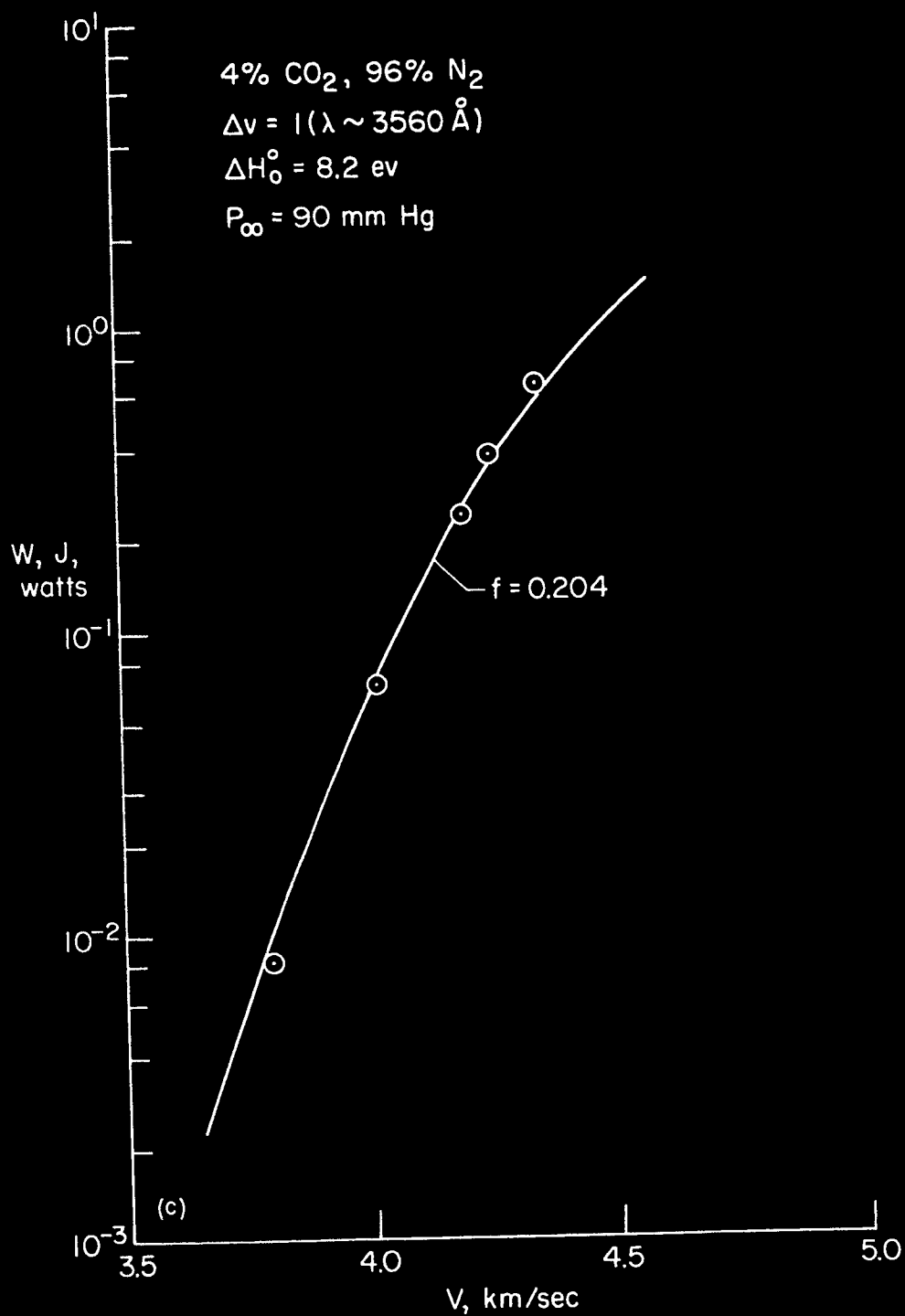


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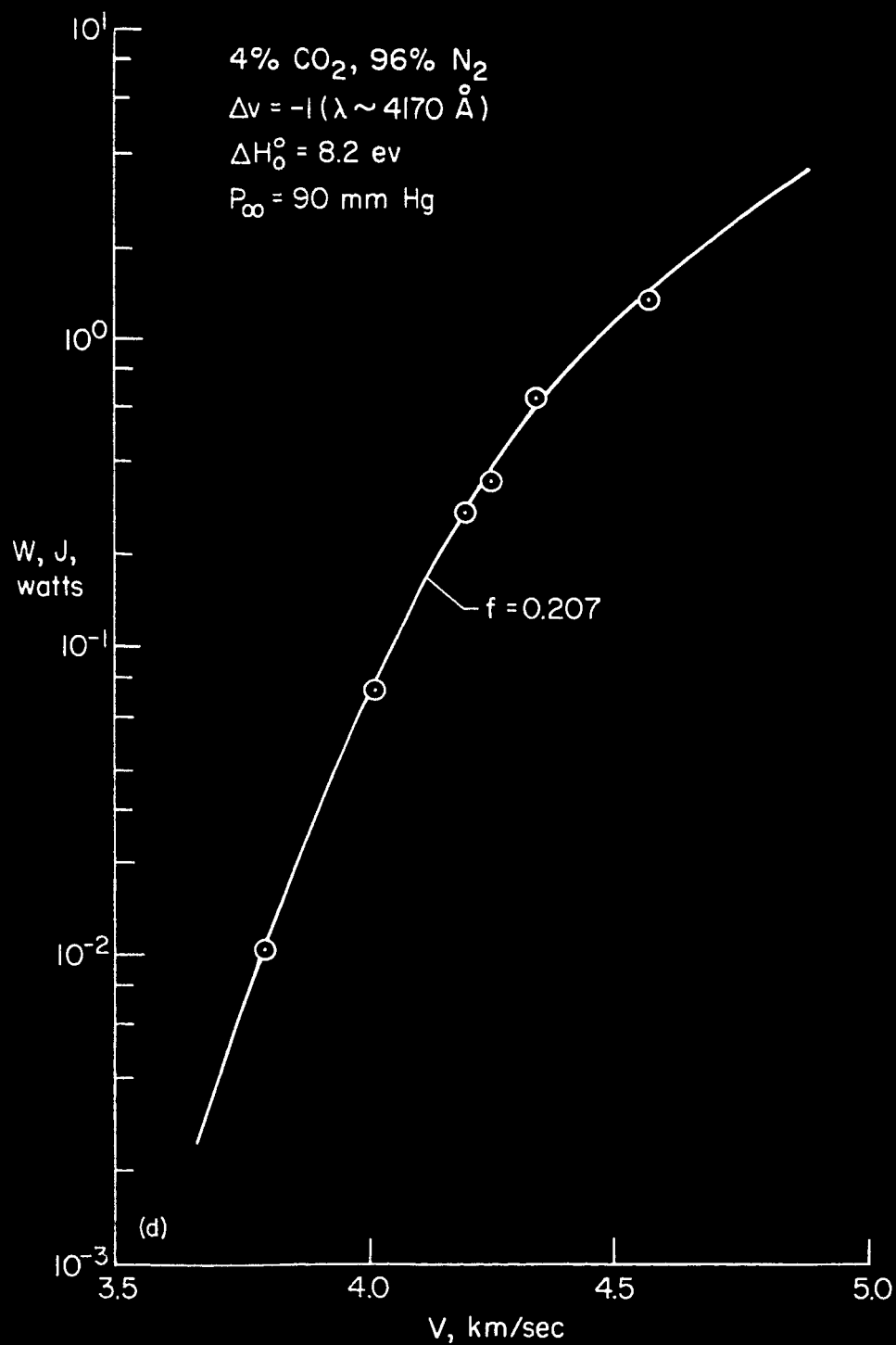


Fig. 4.- Concluded.

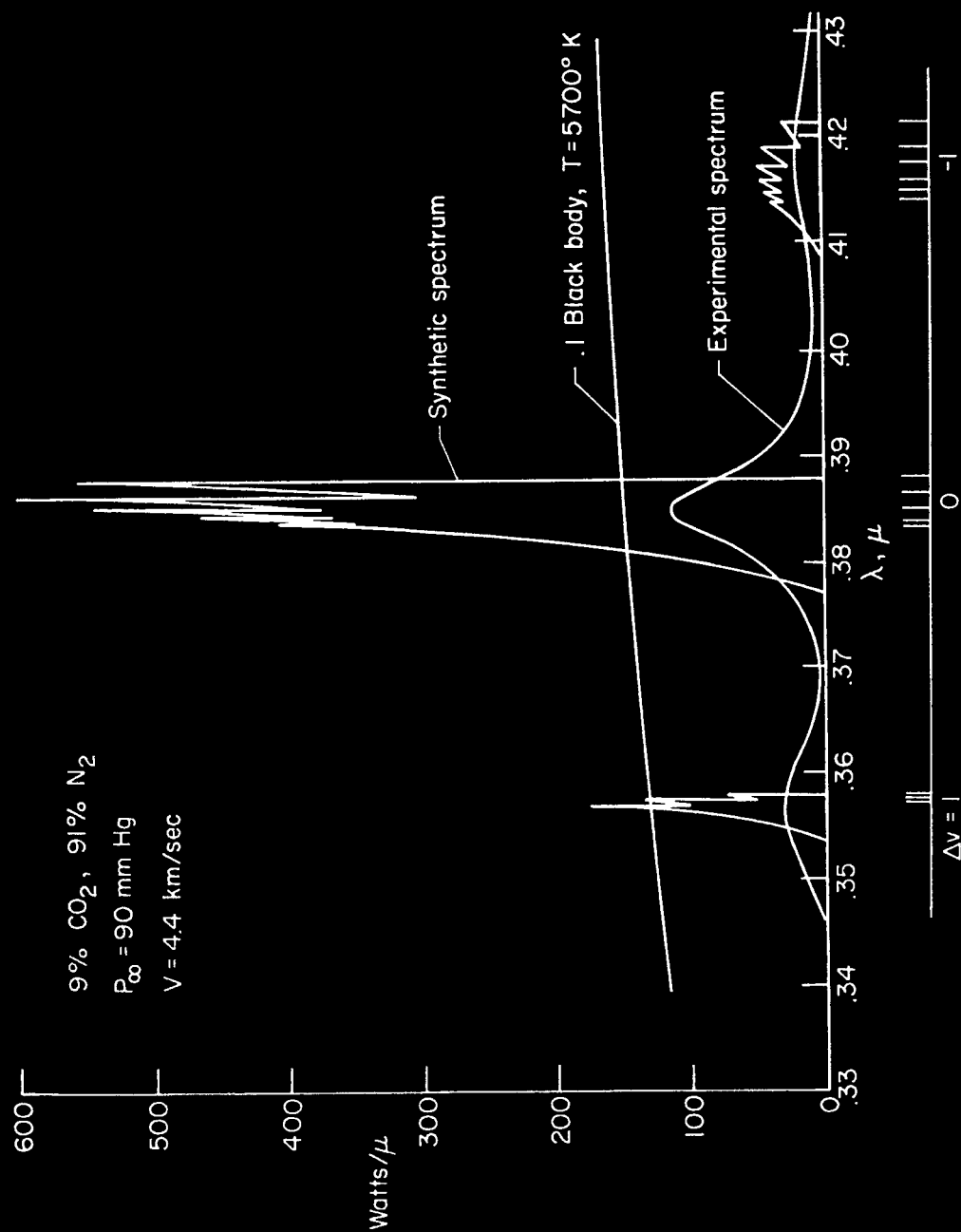


Fig. 5.- Comparison of experimental and synthetic spectra.

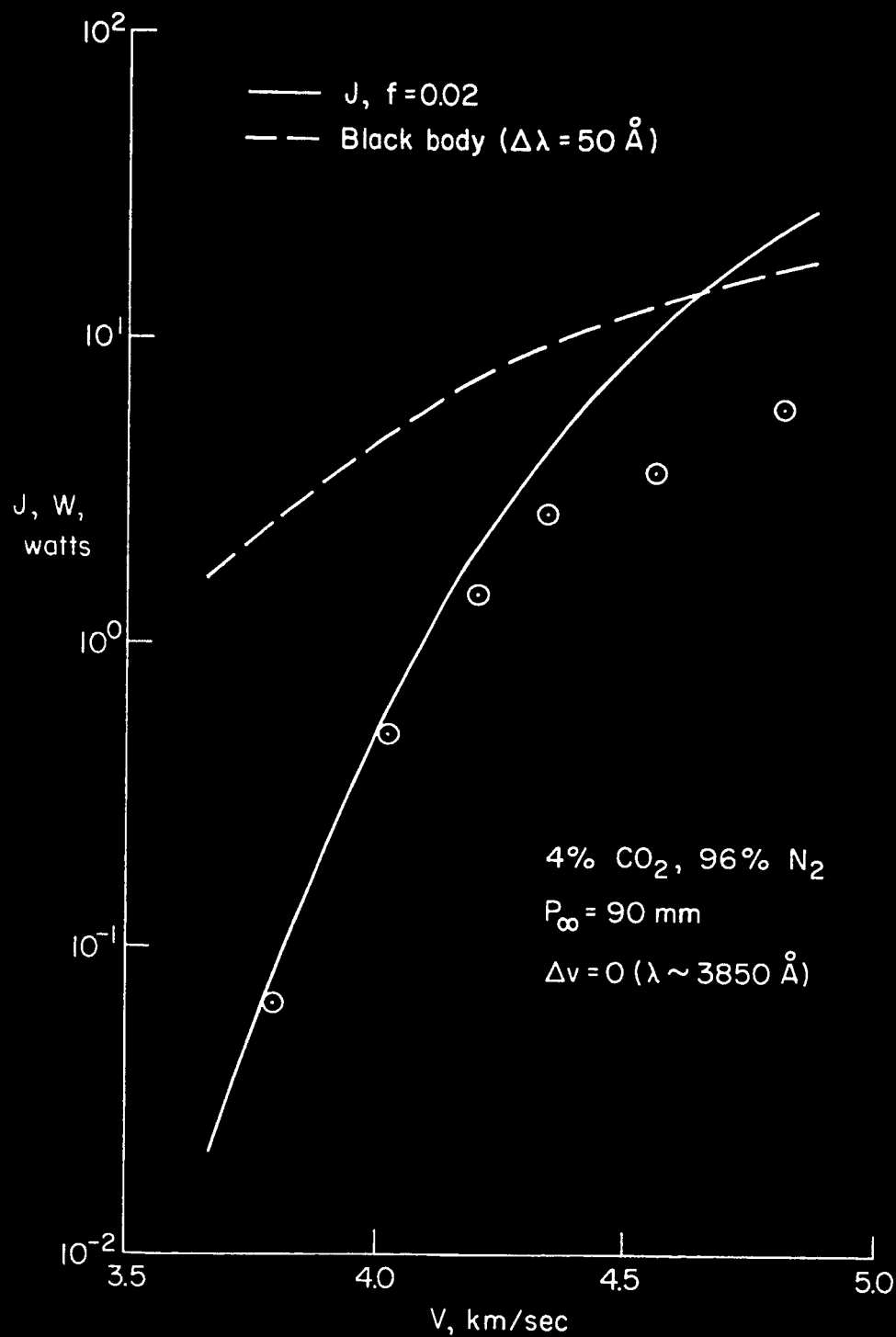


Fig. 6.- Effect of self-absorption on radiation observed by spectrometer for the $\Delta v = 0$ sequence.

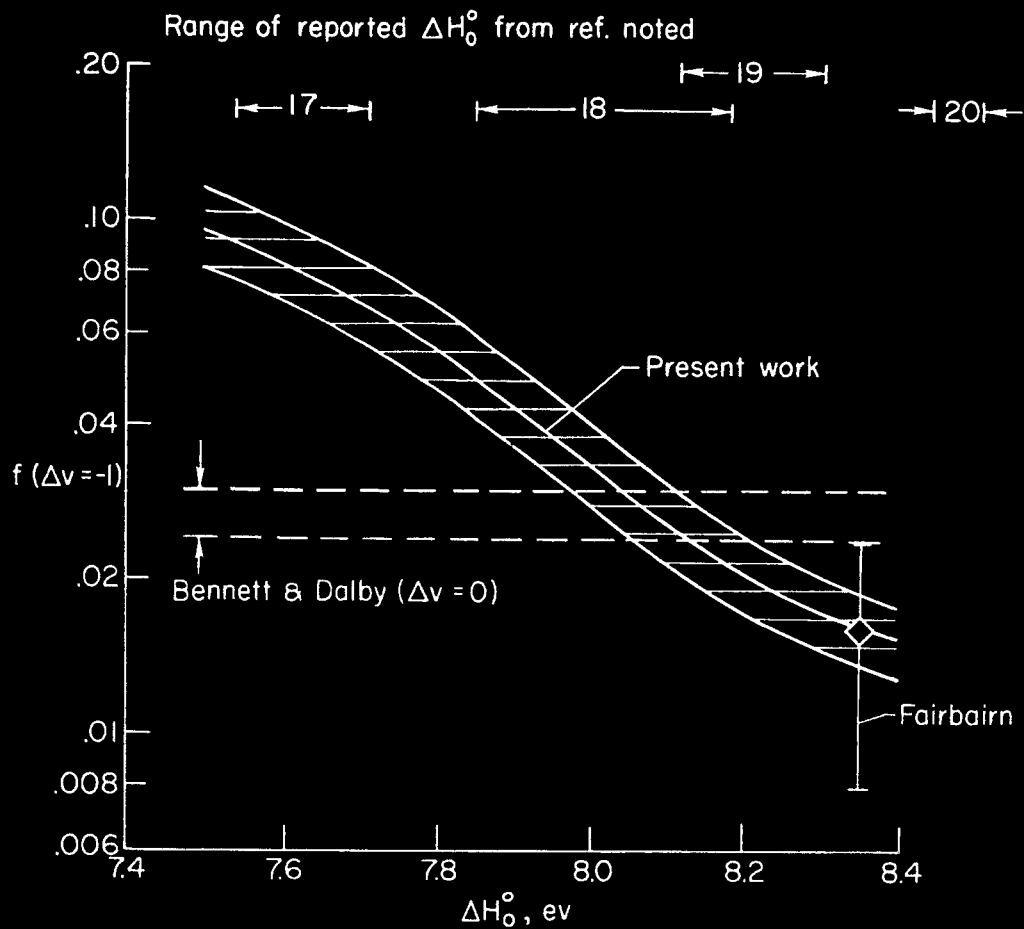


Fig. 7.- Variation of measured f-number as a function of assumed heat of dissociation of CN for the $\Delta v = -1$ ($\lambda \sim 4170 \text{ \AA}$) band sequence.

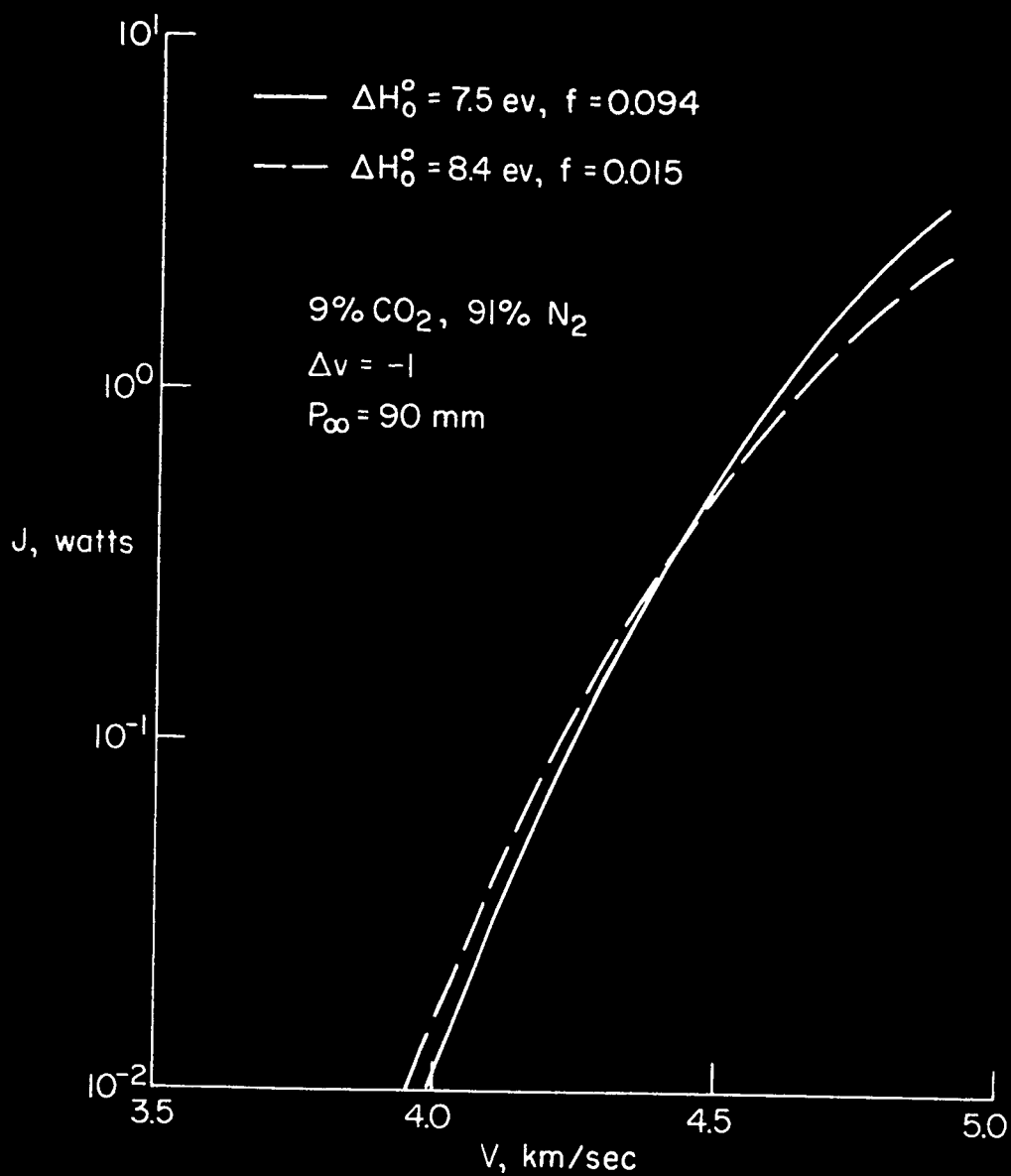


Fig. 6.- Effect of assumed ΔH_0° on the shape of the J versus V curve.

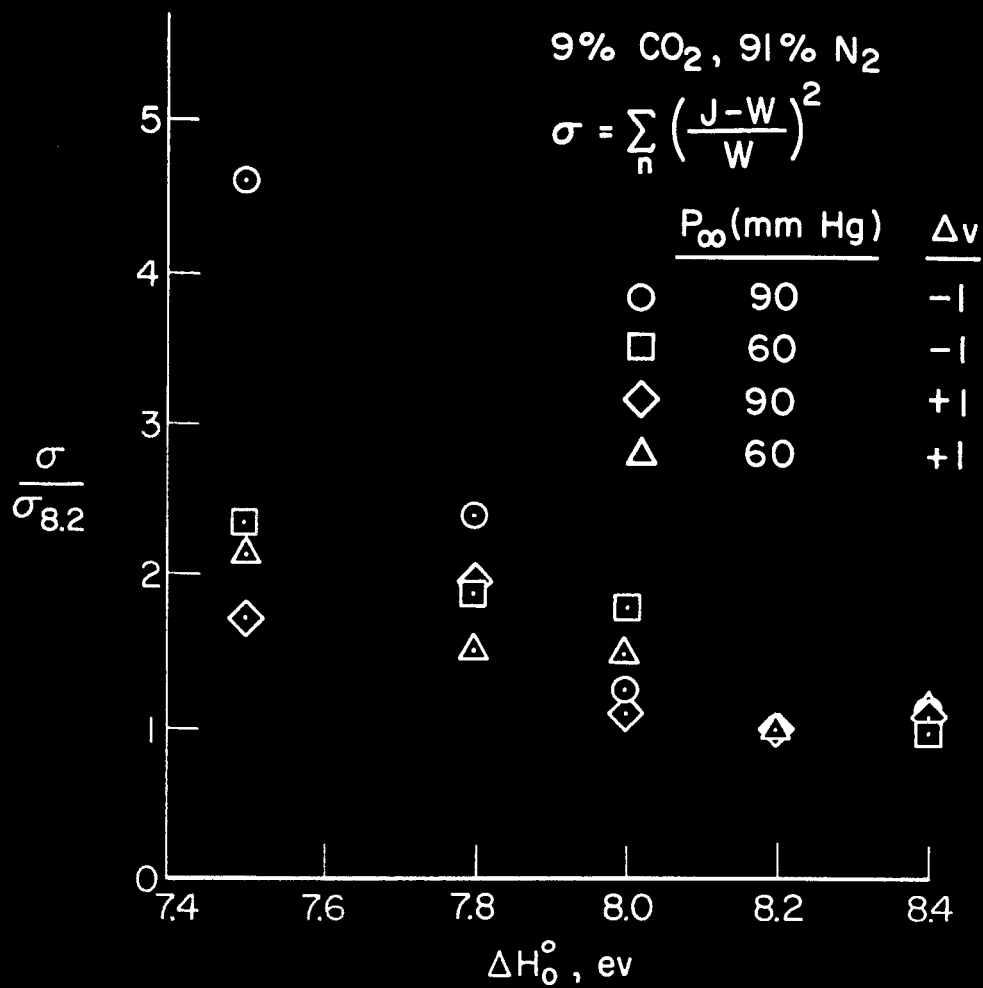


Fig. 9.- Relative quality of the fit of J versus V to the data as a function of assumed ΔH_0° .